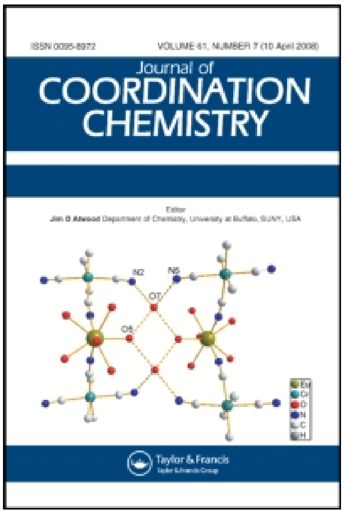

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopic and magnetic properties of three dinuclear copper(II) complexes [Cu$_2$(2-amino-4-methylpyrimidine)$_4$(OH)$_2$](X)$_2$, where X = , or

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To cite this Article Nassirinia, Nassim , Shahmoradi, Ghasem , Sadeghy, Nasrin and Amani, Saeid(2007) 'Synthesis, spectroscopic and magnetic properties of three dinuclear copper(II) complexes [Cu$_2$(2-amino-4-methylpyrimidine)$_4$(OH)$_2$](X)$_2$, where X = , or ', Journal of Coordination Chemistry, 60: 23, 2581 — 2587, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970701286250

URL: http://dx.doi.org/10.1080/00958970701286250

Journal of Coordination Chemistry
Vol. 60, No. 23, 1 December 2007, 2581–2587

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Synthesis, spectroscopic and magnetic properties of three dinuclear copper(II) complexes $[Cu_2(2\text{-amino-4-methylpyrimidine})_4(OH)_2](X)_2$, where $X = NO_3^-$, ClO_4^- or $CF_3SO_3^-$

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(*Received 12 December 2006; in final form 2 January 2007*)

Our main objective is a better understanding of spin–spin interactions of dinuclear copper(II) complexes through bridging systems. Three complexes $[Cu_2(L)_4(OH)_2](X)_2$, where L is 2-amino-4-methylpyrimidine and $X = NO_3^-$, ClO_4^- or $CF_3SO_3^-$ have been synthesized. The compounds are of dinuclear units with hydroxo-bridging groups. All complexes were synthesized in a one-step reaction, and characterized by elemental analysis, FTIR and electronic spectra and by magnetic properties. The compounds exhibit antiferromagnetic interactions at room temperature. The UV–Vis spectra show three absorption bands attributed to d–d transitions of copper(II), ligand → metal charge and $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of ligand. The FTIR spectra indicate Cu_2O_2 ring vibrations in 570–400 cm^{-1} range. The magnetic properties of $[Cu_2(L)_4(OH)_2](ClO_4)_2$ have been investigated in 5–265 K range and the singlet–triplet energy gap of $-240\ cm^{-1}$ was observed.

Keywords: Dinuclear copper(II) complexes; Dihydroxo-bridged; Spin–spin interaction and spin-exchange coupling

1. Introduction

Spin–spin coupling in polynuclear copper(II) complexes remains of considerable interest [1–5]. The structure and magnetic properties of hydroxo-bridged polynuclear transition–metal complexes have been studied extensively [6, 7], with considerable interest in the synthesis, structural, spectroscopic and magnetic properties of oxygen-bridged dinuclear copper(II) complexes [8–13]. The structural and magnetic properties of many oxygen-bridged copper(II) dinuclear complexes containing the Cu_2O_2 bridging system have been investigated previously, in an effort to understand the factors influencing spin–spin interactions [14–17]. Hodgson and co-workers first showed the relation between a structural factor and magnetic coupling of dinuclear copper(II) complexes. The experimental data of many dihydroxo-bridged copper(II) complexes

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701286250

showed a linear relationship between the Cu–O–Cu angle and the J-value, where $-2J$ is the singlet$-$triplet energy gap [18–20]. This relation was theoretically interpreted in term of extended Huckel MO by Hoffmann *et al.* and Kahn [21, 22]. However other structural factors such as planarity of Cu_2O_2 ring and the dihedral angle formed by two coordination planes, have been obtained by several researchers to determine the spin–spin interaction through the bridging system [23–25]. Dinuclear copper(II) sites play an important role in biological metalloproteins [26]. The best investigated dinuclear copper(II) proteins are hemocyanin [27], tyrosinase [28, 29] or catecholase [30]. Despite a vast number of experimental and theoretical studies, our understanding of the magnitude of the copper–copper coupling is still imperfect. We have been interested in the effects of OH group on the change in the magnetic properties. In the present study three dinuclear copper(II) complexes are reported with 2-amino-4-methylpyrimidine (hereafter abbreviated L) of general formula $[Cu_2(L)_4(OH)_2](X)_2$, where $X = NO_3^-$, ClO_4^- or $CF_3SO_3^-$ (scheme 1).

2. Experimental

2.1. *Chemicals*

All chemicals were of reagent grade, purchased from Merck Chemical Company and used as received without further purification.

2.2. *Physical measurements*

C, H and N measurements were obtained by Microanalytical Laboratories of Chemnitz University, Germany. Cu determination was carried on a Perkin-Elmer Atomic Absorption spectrophotometer at Arak University. Electronic spectra were determined on a Perkin-Elmer Lamda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. FTIR spectra were performed in the range of 4000–300 cm^{-1} on a Perkin-Elmer Paragon 1000 FTIR spectrophotometer as KBr pellets. X-band electron paramagnetic resonance spectra were recorded on powder and solutions of complexes both at room and liquid nitrogen temperatures on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibilities were measured in the temperature range 5$-$265 K on a Manics DSM$-$8 susceptometer. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants [31]. A magnetic susceptibility balance of Johnson Matthey Alfa products was used to measure the room temperature magnetic moment.

2.3. *Preparation of the complexes*

Coordination compounds were prepared according to the following general procedure.

$[Cu_2(L)_4(OH)_2](ClO_4)_2$, (C1): Four mmol of 2-amino-4-methylpyrimidine and one mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ were each dissolved in 25 mL of ethanol. The copper solution was then added to the ligand solution and the mixture was placed in a

100 ml flask. After a week, the violet solid was colleted by filtration, washed with ethanol. Yield ca 80%. Elemental analysis for **C1**; Found: C, 30.5; H, 3.6; N, 21.3; Cu, 16.3. Calcd: C, 30.16; H, 3.80; N, 21.10; Cu, 15.96.

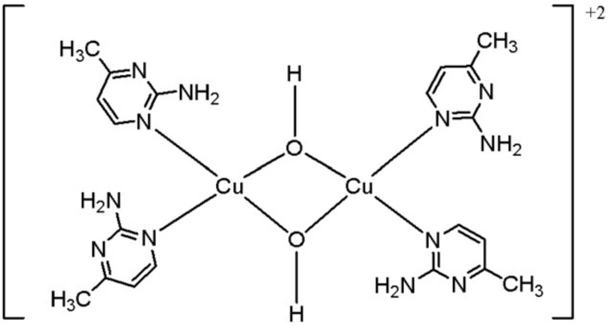
$[Cu_2(L)_4(OH)_2](NO_3)_2 \cdot H_2O$, (C2): Complex **C2** was obtained by similar procedure to that for **C1**, using copper(II) nitrate trihydrate as copper salt. Elemental analysis for **C2**; Found: C, 32.8; H, 4.2; N, 25.9; Cu, 17.4. Calcd: C, 32.48; H, 4.36; N, 26.51; Cu, 17.18.

$[Cu_2(L)_4(OH)_2](CF_3SO_3)_2 \cdot H_2O$, (C3): Compound **C3** was prepared by a similar method as reported for **C1**, using copper triflate. Elemental analysis for **C3**; Found: C, 29.5; H, 3.4; N, 18.0; Cu, 18.6. Calcd: C, 28.92; H, 3.53; N, 18.39; Cu, 18.91.

3. Results and discussion

3.1. *Electronic spectra*

The electronic spectra of all compounds were obtained in solid state as diffuse reflectance and are very similar, illustrating similar geometry. As shown in table 1, the complexes display a band between 580–640 nm, attributed to the d–d transition for CuN_2O_2 chromophore [32, 33]. The second absorption band appears in the range of 380–420 nm assigned to charge transfer from non-bonding orbital of bridging oxygen atoms to the vacant copper(II) d orbitals [34]. The last absorption band found at about 280 nm, is associated with $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the ligand [35].



Scheme 1. Proposed structure for $[Cu_2(2\text{-amino-4-methylpyrimidine})_4(OH)_2]^{+2}$.

3.1. *Magnetic properties*

Magnetic susceptibility measurements were determined from 5 to 265 K on a Manics-8 susceptometer. The susceptibility data were corrected for the magnetization of sample holder and constituent atoms by using Pascal constant. The graphical magnetic properties of **C1** at various temperatures are shown in figures 1 and 2 as μ_{Cu} vs. T or χ_{Cu} vs. T, respectively. The magnetic moment decreases as temperature is lowered, characteristic of spin–spin interaction through a bridging system [36].

Table 1. Spectroscopic data for all three complexes.

Complex	Absorption (nm)	IR (OH) (cm^{-1})	IR (anion) (cm^{-1})	IR (Cu–O) (cm^{-1})	ESR powder	ESR solution DMF	μ_{Cu} (R.T.) B.M.
C1	639, 386, 283	3640	1149,1106, 1063, 626	575, 530	$g = 2.05$	$g_{\parallel} = 2.31$ $g_{\perp} = 2.09$ $A_{\parallel} \approx 160$ $A_{N\parallel} \approx 15$	1.10
C2	582, 430, 282	3548	1420, 1384, 1352, 1047, 780	574, 397	$g = 2.05$	$g_{\parallel} = 2.31$ $g_{\perp} = 2.09$ $A_{\parallel} \approx 160$ $A_{N\parallel} \approx 15$	1.25
C3	604, 418, 283	3560	1149, 1106, 1063, 625	562, 454	$g = 2.06$	– $g_{\parallel} = 2.31$ $g_{\perp} = 2.07$ $A_{\parallel} \approx 158$ $A_{N\parallel} \approx 15$	1.30

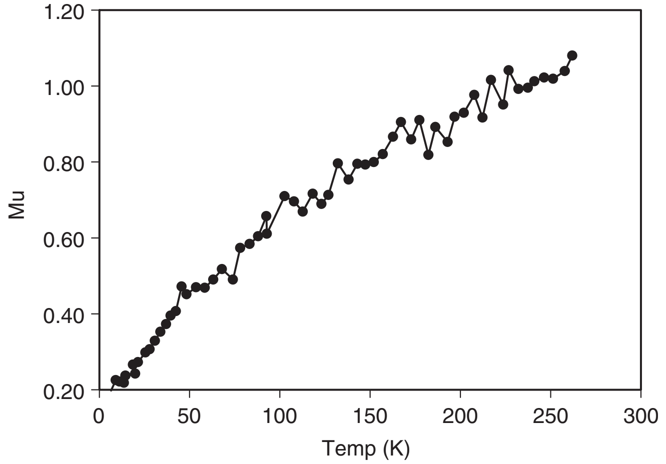


Figure 1. A plot of magnetic moment vs. temperature for complex **C1**.

The corrected susceptibility were fitted by using the modified Bleaney–Bowers equation for exchange-coupled pairs of copper(II) ions [37]

$$\chi_{\mathrm{m}} = \left(\frac{2N^2g^2b^2}{kT}\right)\left[3 + \exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho) + \chi_{\rho} \times \rho \tag{1}$$

$$H_{\mathrm{ex}} = -2JS_1S_2 \tag{2}$$

where is the percentage of paramagnetic impurity in the sample, N, g, β, k and T have their usual meanings. The singlet-triplet energy gap ($-2J$) is defined by Hamiltonian (2). The fitting converged at $-2J = 240\,\mathrm{cm}^{-1}$ and $g = 2.05$ with $\rho = 2.30 \times 10^{-2}$ c.g.s. units. All complexes are dimeric with the room temperature magnetic moment between 1.10–1.30 BM per copper, which appears to be low for a d^9 configuration, so there must be a strong spin–spin interaction through the bridging ligands. Since HO^- is a small ligand, we expect the Cu–Cu distance to be short in comparison with other bridging

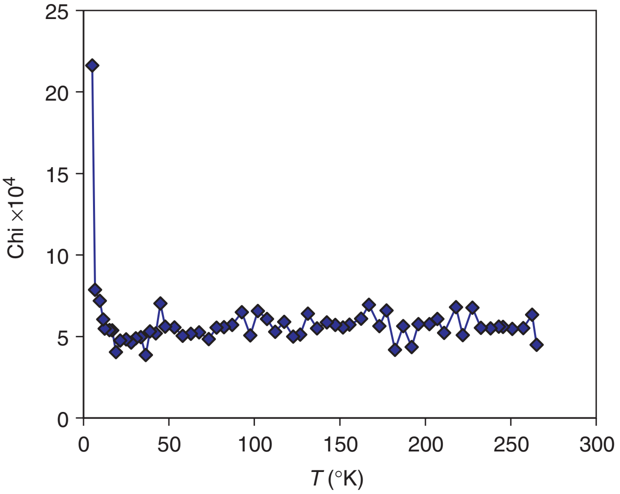


Figure 2. A plot of Chi vs. temperature for **C1**.

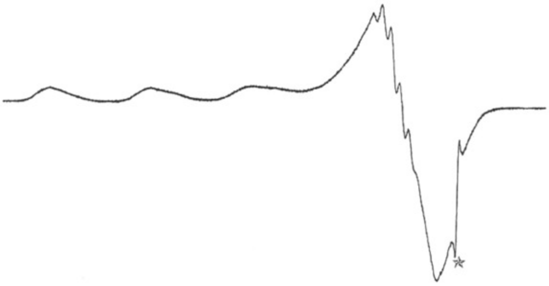


Figure 3. Frozen solution (77 K) ESR X-band spectra for complex **C1**. (⋆) denotes DPPH marker ($g = 2.0036$).

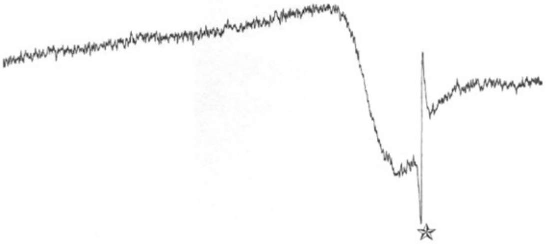


Figure 4. The powder ESR X-band spectra for complex **C1** at room temperature. (⋆) denotes DPPH marker ($g = 2.0036$).

ligands for copper(II) complexes and observe lower magnetic moments for these complexes. In order to provide further supporting evidence for the presence of strong antiferromagnetic interaction, X-band powder and frozen solution ESR spectrum of all complexes were obtained at liquid nitrogen and room temperatures. Figures 3 and 4 show ESR spectra of **C1** at liquid nitrogen and room temperature. In the solid state, the spectra were very similar and appear to be ESR silent with only a weak signal of a monomeric impurity ($g = 2.05$) seen. No half-field forbidden transition was detected in liquid nitrogen or room temperatures. The frozen solution ESR spectra of all complexes in DMF or DMSO show dissociation when dissolved. The mononuclear copper(II) complex has a $g_\perp$ value of 2.09 and $g_\parallel$ of about 2.30 with $A_\parallel \approx 158$ gauss and $A_{N\parallel} \approx 15$ gauss. The presence of five peaks for nitrogen super-hyperfine structure for the complexes agrees with two N donors per copper(II) ion [38, 39].

3.2. *Infrared spectra*

The infrared spectra of the free ligand and the complexes were obtained in the range of 4000–300 cm^{-1}. The IR of the OH, Cu_2O_2 and anion vibrations are of particular interest. All bands that are present in the free ligand are also observed in the spectrum of the complex. In addition, bands at 1139, 1099, 1057 and 626 cm^{-1} for **C1** are assigned to non-coordinated perchlorate [40]. Complex **C2** has addition bands at 1420, 1384, 1352, 1047 and 780 cm^{-1}, attributed to ionic nitrate [41]. For **C3** addition bands 1149, 1106, 1063 and 625 cm^{-1} are assigned to non-bonded $CF_3SO_3^-$ anion [39]. All compounds exhibit two bands with medium intensity between 575–400 cm^{-1}, attributed to copper–oxygen antisymmetric and symmetric vibrations [42–45].

4. Conclusion

Three *bis*-(μ-hydroxo)−bridged dinuclear copper(II) complexes have been made in a one-step synthesis and spectroscopically characterized. All complexes show a subnormal magnetic moment (between 1.10−1.30 BM per copper at room temperature) suggesting an antiferromagnetic spin-exchange interaction within each molecule. The X-band ESR spectra in DMF or DMSO glass (77 K) show $g_\perp$ of 2.09 and $g_\parallel$ of about 2.30 with $A_\parallel \approx 158$ gauss and $A_{N\parallel} \approx 15$ gauss, typical of monomeric tetrahedral copper(II) complexes with $d_{x^2-y^2}$ ground state.

Acknowledgements

The authors would like to thank the Research Council of Arak University for financial support of this research. The authors would also like to appreciate Chemistry Institute and DAAD Organization in Chemnitz University in Germany for the services, facilities and physical measurements. Thanks are also due to Prof. Dr J. Reedijk and G.A. van Albada Leiden Institute of Chemistry, Leiden University, The Netherlands, for chemicals, variable temperature, magnetic susceptibility and physical measurements.

References

[1] R. Veit, J.J. Girrid, O. Kahn, F. Roberts, Y. Jeanin. *Inorg. Chem.*, **25**, 4175 (1986).
[2] J. Sletten, A. Sorensen, M. Yulve, Y. Jourmaux. *Inorg. Chem*, **29**, 5054 (1990).

[3] M.M. Olmstead, W.K. Musker, L.W. Ter Har, W.E. Hatfield. *J. Am. Chem. Soc.*, **104**, 6627 (1982).
[4] W. Haase. *J. Mol. Catal.*, **23**, 331 (1984).
[5] J. Koningsbruggen, E. van Muller, J.P. Haasnoot, J. Reedijk. *Inorg. Chim. Acta*, **208**, 37 (1993).
[6] W.R. McWhinni. *J. Inorg. Nucl. Chem.*, **27**, 1063 (1965).
[7] N.T. Watkins, D.Y. Jeter, W.E. Hatfield, S.M. Homer. *J. Chem. Soc., Faraday Trans.*, **67**, 2532 (1972).
[8] H. Okawa, M. Koikawa, S. Kida. *J. Chem. Soc., Dalton Trans.*, 469 (1990).
[9] P.L. Burk, J.A. Osborn, M.T. Youinou. *J. Am. Chem. Soc.*, **103**, 1273 (1981).
[10] D.M. Haddleton, A.J. Clark, D.J. Duncalf, A.M. Heming, D. Kukulj, A.J. Chopoter. *J. Chem. Soc. Dalton Trans.*, 381 (1998).
[11] P.K. Coughlin, S.J. Lippard. *J. Am. Chem.. Soc.*, **103**, 3228 (1981).
[12] N. Kitajina, Y. Mori-oka. *Chem. Rev.*, **94**, 737 (1994).
[13] M.S. Haddad, D.M. Hendrickson. *Inorg. Chim. Acta*, **28**, L121 (1978).
[14] L. Banci, A. Bencini, D. Gatteschi, C. Zanchini. *J. Mag. Reson.*, **48**, 9 (1982).
[15] L. Banci, A. Bencini, D. Gatteschi. *J. Am. Chem. Soc.*, **105**, 761 (1983).
[16] A. Bencini, D. Gatteschi, C. Zanchini. *Inorg. Chem.*, **24**, 700 (1985).
[17] G. Bernardinelli, A. Kubel-Pollak, S. Ruttimann, A.F. Williams. *Chimia*, **46**, 155 (1992).
[18] D.J. Hodgson. *Prog. Inorg. Chem.*, **19**, 173 (1975).
[19] W.H. Crawford, H.W. Richardson, J.R. Wasso, D.J. Hodgson, W.E. Hatfield. *Inorg. Chem.*, **15**, 2107 (1976).
[20] L. Erz, W. Haase. *J. Chem. Soc. Dalton Trans.*, 875 (1980).
[21] P.J. Hay, J.C. Thibeault, R. Hoffmann. *J. Am. Chem. Soc.*, **97**, 488 (1975).
[22] O. Kahn. *Inorg. Chim. Acta*, **62**, 3 (1982).
[23] M. Mikuriya, K. Toriumi, T. Ito, S. Kida. *Inorg. Chem.*, **24**, 629 (1985).
[24] G.D. Fallon, K.S. Murray, W. Mazurek, M.J. O'Conner. *Inorg. Chim. Acta*, **96**, 53 (1985).
[25] W. Mazurek, B.J. Kennedy, K.S. Murray, M.J. O'Conner, J.R. Rodgers, M.R. Snow, A.G. Weds, P.R. Zwack. *Inorg. Chem.*, **24**, 3258 (1985).
[26] E.I. Solomon, M.J. Baldwin, M.P. Lowery. *Chem. Rev.*, **92**, 521 (1992).
[27] K.A. Magnos, H. Tom-That, J.E. Carpender. *Chem. Rev.*, **94**, 727 (1994).
[28] N. Kitajima, Y. Moro-Oka. *Chem. Rev.*, **94**, 737 (1994).
[29] E.I. Solomon, U.M. Sundaram, T.E. Mackokin. *Chem. Rev.*, **96**, 2563 (1996).
[30] D. Meiwes, F. Zippel, H.F. Nolting, C. Hermes, B. Krebs, H. Witzel. *J. Inorg. Biochem.*, **59**, 715 (1995).
[31] I.M. Kolthoff, P.J. Elving. *Treatise on Analytical Chemistry*, Part 1, Vol. 4, Interscience Publ.m, New York (1963).
[32] B.J. Hathaway. *Struct. Bonding*, **57**, 56 (1984).
[33] A. Bencini, D. Gattaeschi, C. Zanchini, W. Haase. *Inorg. Chem.*, **24**, 3485 (1984).
[34] M. Mikuraya, H. Okawa, S. Kida. *Bull. Chem. Soc. Jpn*, **53**, 3717 (1980).
[35] L. Casella, O. Carugo, M. Mullotti, S. Garofani, P. Zannello. *Inorg. Chem.*, **32**, 2056 (1993).
[36] G. Tabbi, W.L. Driessen, J. Reedijk, R.P. Bonomo, N. Veldman, A.L. Spek. *Inorg. Chem.*, **36**, 1168 (1997).
[37] B. Bleaney, K.D. Bowers. *Proc. R. Soc. London, Ser. A*, **214**, 541 (1952).
[38] S. Amani, G.A. Albada, I. van Mutikainen, U. Trupinen, J. Reedijk. *Polyhedron*, **14**, 1991 (1999).
[39] S. Amani, G.A. Albada, H. van Kooijman, A.L. Spek, J. Reedijk. *Inorg. Chim. Acta*, **286**, 24 (1999).
[40] B.J. Hathaway, I.M. Procter, R.C. Slade, A.A.G. Tomlison. *J. Chem. Soc.*, 2219 (1969).
[41] B.J. Hathaway, D.G. Holah, M. Hudson. *J. Chem. Soc.*, 4586 (1963).
[42] G.A. Albada, S. van Amani, H. Kooijman, A.L. Spek, J. Reedijk. *Inorg. Chim. Acta*, **287**, 22 (1999).
[43] S. Amani, N. Sadeghy, Z. Talebi. *J. Chem. Soc. Pak.*, **4**, 271 (2000).
[44] M. Dadpu, A.R. Mahjoob, S. Amani. *Iran. J. Chem. & Chem. Eng.*, **1**, 37 (2003).
[45] N. Sadeghy, S. Amani. *Polish J. Chem.*, **79**, 1749 (2005).